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COMMUNICATION

Ionic *N*-Phenylpyridinium Tetracatenar Mesogens: Competing Driving Forces in Mesophase Formation and Unprecedented Difference in Phase Stabilisation within an Homologous Series

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Ionic, tetracatenar liquid crystals containing an *N*-phenylpyridinum core are described; many of these compounds display a SmA phase, something extremely rare in tetracatenar materials. The competing forces driving mesophase formation lead to an unprecedented difference in phase stabilities for SmA and Col_h phases.

Ionic liquid crystals (ILCs)[1] are one of the oldest classes of liquid crystals and have recently become popular in parallel with the growth of interest in ionic liquids. The promise of the advantageous combination of the properties of ionic liquids with the long-range order inherent in liquid crystals makes them attractive materials. For example, we have shown how ILCs can act as solvents to influence the stereochemical outcome of reactions,[2] while temperature-driven, mesophase-dependent conductivity has been reported by Kato and co-workers.[3] The conductivity in this latter example is controlled by a mesophase transition highlighting the fact that control over these desirable physical properties requires a fundamental understanding of the factors controlling phase behaviour.

The factors that drive liquid crystal phase formation are many and their interplay can be extremely subtle, a particularly topical example of which is the simple parity of a flexible chain linker which drives very substantial changes in mesomorphism.[4] Polycatenar liquid crystals[5] – mesogens with extended rod-like cores and three or more terminal chains – are a good example where subtle effects dominate. In particular, tetracatenar mesogens with two chains at each end of the rod, are of interest as short-chain examples show nematic and/or SmC phases while longer-chain homologues show columnar hexagonal phases. Their mesomorphism is driven largely by the change in relative volume between the core and terminal chains, and has been discussed extensively.[6] Some years ago, formally ionic polycatenar complexes of silver(I) (Fig. 1) were reported and their behaviour largely mirrored that of neutral analogues.[7]

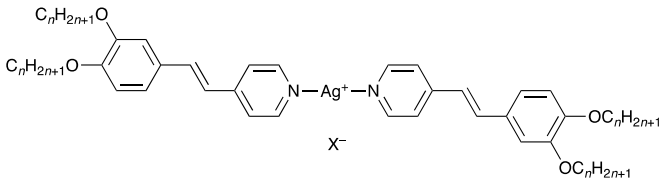

Figure 1. Structure of the tetracatenar silver(I) stilbazole complexes.

Despite being formally ionic, conductivity showed them to exist as tight- bound ion pairs, in effect rendering them almost neutral.[8] They were also of interest as their mesomorphism is influenced by external agents. Thus, added hydrocarbons associated with the terminal chains effectively increasing the *chain* volume while small, dipolar, aprotic materials associated with the polar core effectively increasing *its* volume.[9]

While there are examples of truly ionic liquid crystals with several terminal chains, they are typically fan-shaped in nature with a 3,4,5-trialkoxyphenyl group and their mesomorphism is dominated by the appearance of columnar phases.[10] Thus, to date and to the best of our knowledge, there have been no examples of classical polycatenar mesogens that are truly ionic. Keen therefore to understand how the different factors that drive liquid crystal phase formation might tension against one another in these systems, a synthetic programme was initiated to prepare and investigate examples of such materials.

The compounds selected for study are based on the *N*-phenylpyridium cation, which has been used extensively by Coe and co-workers in studies of optically non-linear Ru^{II} complexes.[11] In the synthetic route (Scheme 1), the first important intermediate is the 3,4-dialkoxypyridine **4**-*n*, prepared from a 3,4-dialkoxyphenylboronic acid pinacol ester (**3**-*n*) and 4-bromopyridinium chloride. The key step is the so-called Zincke reaction,[12] a two-step process in which a pyridine is first reacted with 2,4-dinitrochlorobenzene to form *N*-(2,4-dinitrophenyl)pyridinium chloride after which reaction with aniline gives *N*-phenylpyridinium chloride. In this work, the Zincke chemistry uses 4-(3,4-dialkyloxyphenyl)pyridine (**4**-*n*) as

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Electronic Supplementary Information (ESI) available: [Full experimental details and some phase diagrams are found as part of the Supplementary Information. Single crystal structure reference at CCDC is 1893621]. See DOI: 10.1039/x0xx00000x

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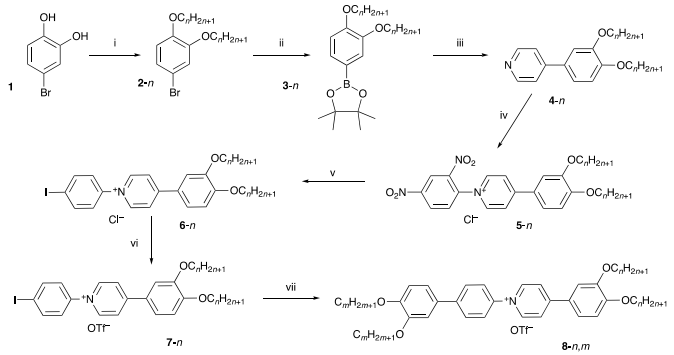

Scheme 1. Synthesis of the target mesogens: (i) $C_nH_{2n+1}Br$, K_2CO_3, acetone, 65 °C; (ii) *bis*(pinacolatodiboron), DMSO, $[PdCl_2(dppf)]$, 80 °C, N_2; (iii) 4-bromopyridine hydrochloride, THF/H_2O, $[Pd_3(OAc)_6]$/SPhos, Na_2CO_3, N_2, 65 °C; (iv) 1-chloro-2,4-dinitrobenzene, acetone, 65 °C; (v) 4-iodoaniline, BuOH, 125 °C; (vi) AgOTf, DMF, 80 °C; (vii) 3,4-dialkoxyphenylboronic acid pinacol ester, THF/H_2O, $[Pd_3(OAc)_6]$/SPhos, 65 °C, N_2.

the substrate, which, after two steps gives the 4-iodopyridiniumsalt (**6**-*n*). The anion of **6**-*n* is then metathesised to the more soluble triflate (**7**-*n*) and the product (**8**-*n,m*) is finally obtained *via* a Suzuki-Miyaura coupling with a 3,4-dialkoxyphenylboronic acid pinacol ester (**3**-*n*).[13] We note in passing that very recently, Wang *et al.* reported mesomorphic *N,N'*-diphenyl-4.4'-bipyridines prepared using a Zincke approach.[14] In this work, the cation structure is symmetric (*n* = *m* and so written simply as **8**-*n*), but the Scheme shows the straightforward access to unsymmetric derivatives. Unlike the silver complexes where vinyl links are found (Fig. 1), the rings in **8**-*n* are joined by σ-bonds. Derivatives of **8** were prepared with vinylic links, but the barrier to visible light-induced *trans*/*cis* isomerisation was extremely low (not the case with the silver complexes) precluding isolation of pure *trans, trans*-isomers.

The transition temperatures for salts **8**-*n* ($8 \le n \le 18$) are collected in Table S1, while a phase diagram is given as Figure 2. The first significant observation is that for the for the homologues where $8 \le n \le 13$,[15] the mesophase observed is the SmA phase, characterised by its distinctive focal conic fan texture (Fig. 3a). With one exception in a compound with ω-cyanoalkylene chains,[16] this is an otherwise unprecedented observation in tetracatenar liquid crystals, where to date the only smectic phase seen has been the SmC. Then, as the terminal chain length changes from 13 to 14, the phase behaviour switches and a Col_h phase (see below) is observed (Figure 3b), although it should be noted that the Col_h-to-Iso temperatures are affected by decomposition, observed in the higher reaches of the phase. Interestingly then, there are no homologues that show what might be termed 'crossover' behaviour – *i.e.* showing both a SmA and a Col_h phase or showing an intermediate phase, such as a cubic phase.

In considering the transition temperatures, it is noticeable that the melting point is relatively insensitive to the terminal chain length. This could suggest that it is driven by a breakdown of the ionic lattice, which would be fairly constant across the different homologues. This would then imply that the clearing point reflects the terminal chain length and would contrast with the position taken by Jeffrey[17] in carbohydrate liquid crystals (carbohydrate moieties functionalised with long alkyl chains)

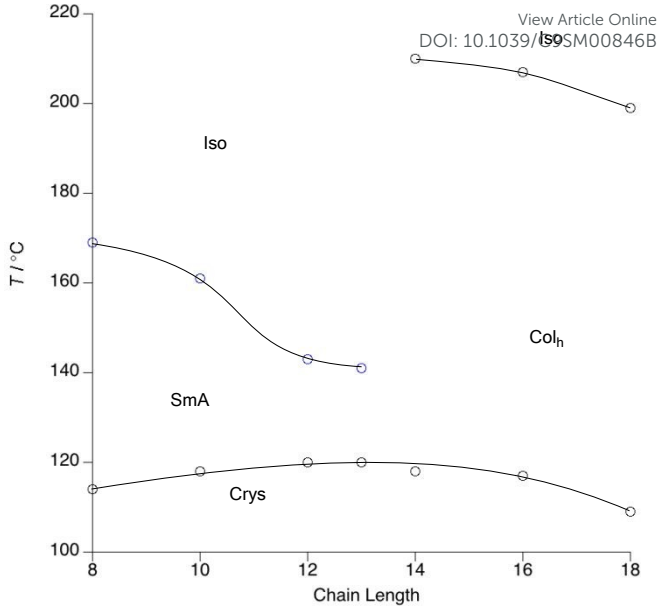

Figure 2. Phase diagram of the tetracatenar pyridinium salts **8**-*n*.

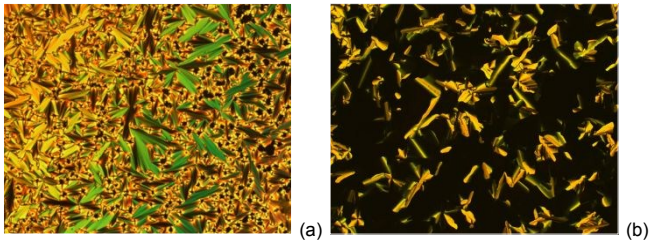

Figure 3. Optical textures taken on cooling of: (a) the SmA phase where *n* = 8; *T* = 162 °C; (b) the Col_h mesophase where *n* = 18; *T* = 163 °C.

where he proposed that the melting point represents a melting of the chains and that clearing is driven by a breakdown of the intermolecular hydrogen bonding network (which would be loosely analogous to the ionic lattice of these new compounds).

Further structural information was obtained using small-angle X-ray scattering. Salts that form SmA phases showed a strong *d*(001) reflection (Fig. 4a) and the spacings (Fig. S1) show a monotonic increase with chain length as expected.

Comparison with the calculated molecular length for the all-*trans* conformation of the cation of **8**-8 (38.9 Å) shows that the observed layer spacing (27.8 Å) is 71% of this value at a reduced temperature of 0.97; similar contractions of the layer spacing were also observed for compounds **8**-10 to **8**-13. However, these materials are ionic, and therefore have associated with them a counter-ion that most probably spends a great deal of time located next to the pyridinium core (see below), which will increase the effective cross-sectional area of the core significantly. Chain folding or interdigitation, which also account for the observation that $d(100) < l$, may then act to fill the space effectively and allow the zero-curvature SmA phase to form.

Figure 5 also shows the lattice parameter, *a*, for the salts that form a Col_h phase, calculated from the observed *d*(10) spacing and once more, a monotonic increase is seen. The homologues with *n* = 16 and 18 also showed the characteristic

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d(11) reflection, whereas for *n* = 14, only a single reflection was observed, which is insufficient to identify the phase as hexagonal. Furthermore, the optical texture obtained by heating and cooling (Fig. S2) was not obviously that of a Col_h phase. Therefore, contact preparations were performed between the *n* = 14 and *n* = 16 homologues, and the two were found to be co-miscible, confirming the phase of the former as Col_h. For completeness, contact preparations between the *n* = 14 homologue and both the *n* = 12 and *n* = 13 homologues were carried out; neither showed any miscibility. The absence of high-order reflections where *n* = 14 is presumably a consequence of less well-developed 2D order in this material, which may well reflect the fact that it is very much at the point where the phase behaviour switches from lamellar to columnar.

Given the observation of a SmA phase in these materials, how might their mesomorphism be rationalised? In general, the mesomorphism of polycatenar mesogens is understood by considering how space is filled, tensioning the volumes of the molecular core and the terminal chains while taking into account the effective cross-sectional areas of the chains and the core at the core-chain interface.[18] In tetracatenar mesogens, that the SmC phase is the only lamellar phase observed can then be understood by recognising that the larger cross-sectional area of the chains and the smaller cross-sectional area of the core can only be matched with a tilted core.[18]

The compounds under investigation here are, however, quite different inasmuch as they have an associated anion. DFT calculations of the electrostatic potential of a model compound with *n* = 1 (Fig. 5) shows that the positive charge is quite well localised on the pyridinium ring and so it is likely that the triflate anion is strongly associated with this area of the cation, which was confirmed by calculation (Fig. S4 and SI). Similarly, single-crystal X-ray diffraction showed the proximity of the anion to the pyridinium ring in the solid state, too (Figure S5). As such, there is a good deal of additional cross-sectional area associated with the core which, when compared to the cross-sectional area of the chains at the core-chain interface, means that there is better compatibility in area between core and chains so suppressing the drive for the cores to tilt and thus allowing the SmA phase to form. Of course, formation of a SmA phase is also the typical behaviour of calamitic, ionic mesogens.

Support for these assertions comes from two related observations. First is work in which the nature of the mesophase in polycatenar liquid crystals can be controlled by the additional of external agents that associate preferentially with either the terminal chains or the core and so influence the core-chain balance. Thus, 'bulking up' the core with appropriate agents leads to phases of reduced curvature.[9] In this case, the anion fulfils a similar role to that of the agent associating with the core and, in addition, creates a greater separation between the chain-bearing cations. The fact that the observed layer spacing is shorter than the length of the cation then allows for either chain folding or interdigitation to fill the additional space consequent on the location of the anion. Second is a rather nice study by Pelzl *et al.* with so-called swallow-tailed liquid crystals which, having four terminal chains, normally show a SmC phase for the same reasons as those advanced for tetracatenar

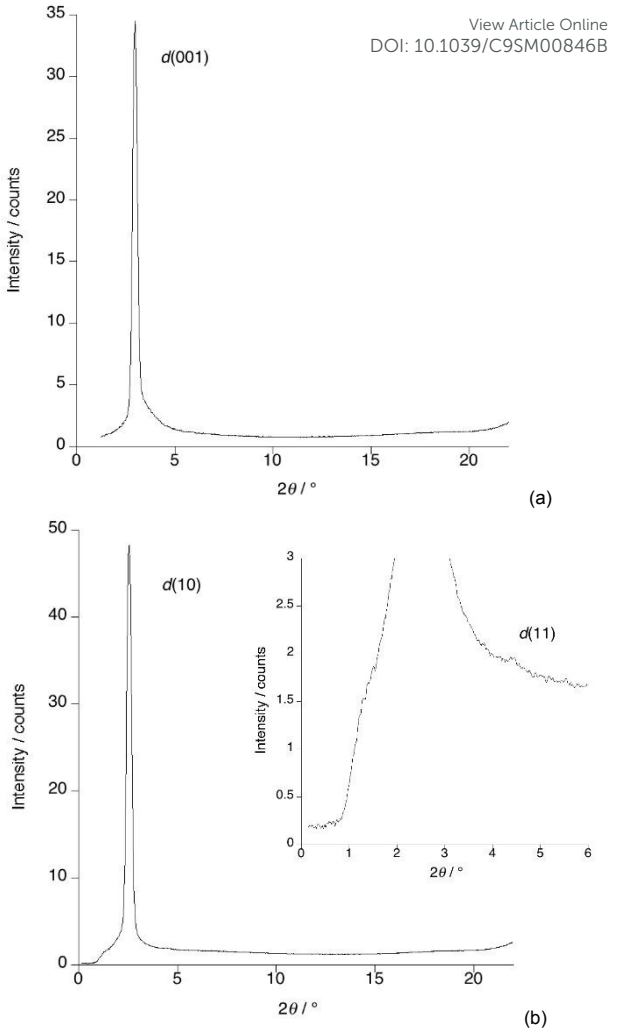

Figure 4. Figure 4 SAXS patterns for: (a) **8**-8 at 139 °C on cooling and (b) **8**-16 at 127 °C on heating (inset shows the *d*(11) reflection).

mesogens. In this study, they doped the neutral swallow-tail compounds with small, calamitic mesogens and in so doing formed an injected SmA phase on account of increasing both the core volume and cross-sectional area (structures of the compounds involved are found in Fig. S3).[19] These observations then support strongly the location of the anion between the cations, which does raise the thought that in addition to the lamellar periodicity, there could be lateral, electrostatic correlations *within* the layers. This could suggest the possibility of biaxial ordering, but none of the photomicrographs (including those in homeotropically aligning cells) implies anything other than a uniaxial SmA phase. Thus, if lateral, electrostatic correlations exist, they are clearly rather short-range in nature.

Finally, there is one very significant question that remains, evident immediately in the phase diagram (Figure 2), namely a pronounced change in clearing point when the mesophase changes from SmA to Col_h. Thus, for **8**-8 to **8**-13 (all SmA), the clearing point decreases from 169 to 141 °C, whereas for **8**-14 to **8**-18, the apparent clearing point decreases from 210 to 199 °C (noting the imprecision inherent in this letter determination owing to decomposition as noted elsewhere). Clearly there is a

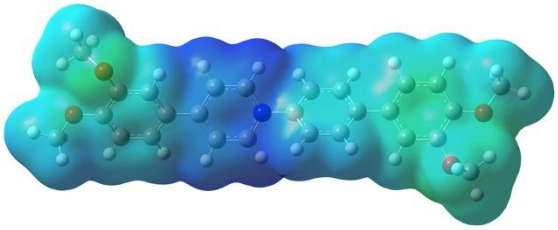

Figure 5. Electrostatic potential map calculated from DFT calculations for the core (*n* = 1). Surface computed for isoval = 0.001, with ESP shading between –0.15 (red) and +0.15 (blue). Method: B3LYP 6-311G(d,p).

very significant difference in the stability of the two mesophases (69 °C between two adjacent homologues) yet with minimal difference in molecular structure and melting point. Inlooking for some analogy, we did find work on neutral analogues (3,3',4,4'-tetraalkoxyquaterphenyls) reported by Sultana *et al.*,[20] but the reported phase behaviour appears in error (Fig. S6 and SI) and so no useful comparison was possible.

In Figures S7 to S9 are plotted phase diagrams for three series of tetracatenar mesogens whose mesomorphism changes to Col_h phase at increasing chain lengths and where a SmC phase is observed at shorter chain lengths. In all of these cases there is a more-or-less smooth decrease in the clearing point, with perhaps something of a levelling-off as the columnar phase is reached. The same observation of mesophase destabilisation with increasing terminal chain length is found in a series of five-ring, tetracatenar mesogens (Fig. S10) where the central ring bears a lateral F, CN, CF_3 or $C_{15}H_{31}$ group.[21] Interestingly, however, Figures S11 and S12 show phase diagrams for tetracatenar silver triflate and dodecylsulfate complexes, respectively, and here there is an *increase* in mesophase stability from the cubic to the columnar phase (there is no SmC phase in these materials). Other examples of this behaviour are found for related tetra- and hexa-catenar complexes, and thus mesophase stabilisation with increasing chain length would seem to be an effect of an anion and not simply a lateral group (Fig. S10 & Ref. 21).[7] So what is the effect being observed? Is it that the columnar phase is stabilised in these circumstances or that phases of lower curvature are destabilised? It is postulated that attendant anions act to destabilise lamellar arrangements and that when the columnar phase is entered, the mode of packing[22] is better able to accommodate the anion, leading to stabilisation. What is, however, unanticipated is the magnitude of this effect as exemplified by the huge change in clearing point between **8**-13 and **8**-14, representing a *very* significant destabilisation of the SmA phase. The synthesis of related materials with other anions is underway to test this hypothesis further.

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Conflicts of interest

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There are no conflicts to declare.

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